Abstract

Herein we report a metal-free, acid initiated living cationic polymerization of 4-methoxystyrene mediated by a methanol additive. A study using alcohols of different nucleophilicity indicated that the molecular weight and dispersity of the synthesized polymers varies inversely with the nucleophilicity of the alcohol additive, with the best control imparted via methanol. Further studies on the effect of the loading of the acid initiator and methanol additive indicate that the molecular weight and dispersity of the synthesized poly(4-methoxystyrene) are controlled by the concentration of methanol rather than concentration of protonic acid initiator. We propose that methanol acts as a reversible chain-transfer agent, analogous to reversible addition fragmentation chain-transfer (RAFT) polymerization, regulating the equilibrium between the propagating active cation chain and the resulting oxonium intermediate. The molecular weights of the synthesized polymers were in good agreement with theoretical molecular weights, assuming that each molecule of methanol generates one polymer chain.

Introduction

The ongoing desire to develop new methods for the synthesis of well-defined polymers with complex molecular architectures has resulted in a renewed interest in living/controlled polymerizations. Recent advances in controlled/living polymerization techniques have enabled the synthesis of materials with controlled structures, sequences, and molecular weights.[1-4] Synthetic strategies for these controlled polymerizations are varied, propagating via radical, coordination, cationic, and anionic species. Despite their different propagating modes, the key step for these living/controlled polymerizations is the reversible deactivation of the active propagating chain end into a dormant species, allowing for control over molecular weight and polymer structure.[5,6]

However, achieving a high degree of control over this interchange between active and dormant species is difficult, particularly in cationic polymerizations.

Cationic polymerization is a type of chain growth polymerization that utilizes a carbocation as the propagating species. These polymerizations are characterized by rapid rates of propagation, greater than that of radical or anionic, as well as an increased sensitivity to solvent effects, trace impurities, and chain transfer of the propagating active site. The high reactivity of the growing carbocation chain and its inherent instabilities cause there to be a greater probability for uncontrolled termination of the polymer chains, making it almost impossible to synthesize structurally well-defined polymers in a "living" fashion.[4] To overcome these challenges and achieve the reversible activation and deactivation process vital to controlled polymerizations, researchers have focused on methods to "control" the side reactions (e.g., chain termination and chain transfer) prevalent in cationic polymerizations.

The first example of living cationic polymerization was reported by Higashimura and Sawamoto in their 1984 paper on the by HI/I_2 catalyzed living cationic polymerization of vinyl ethers.[7,8] This initial report was followed soon after by Faust and Kennedy and the living cationic polymerization of isobutylene.[9] These early discoveries have acted as the basis for the development of living cationic systems whose control is imparted by the introduction of additives. Most of the living cationic polymerization methodologies reported in the literature are mediated by a two-component system consisting of an initiator and a co-initiator.[11-14] Since the discovery of HI/I_2 catalyzed living cationic polymerizations, a wide variety of Lewis acids and Bronsted acids have been used as co-initiators.[7-8,14] The initiation step for the living cationic polymerization of vinyl monomers is done in two parts. A protonic acid, such as HCl or HI is used to initiate the propagating carbocation center through markovnikov addition across the double bond of the vinyl monomer, resulting in the formation of an acid adduct.[15-29] Lewis acids such as I_2 and ZnI_2 and

ammonium salts with non-nucleophilic anions such as PF_6^-, BF_4^-, and $CF_3SO_3^-$, also known as activators, are then required to activate the labile carbon halogen bond present in the acid adducts which generates the propagating carbocation site (**Figure 1**).[7,19-22] The use of a strong activator requires the addition of a Lewis base to mediate the polymerization and stabilize the growing polymer chain, as does the use of a strong acid, such as CF_3SO_3H and H_3PO_4, to initiate the polymerization.[24-26] While these tunable initiating systems allow for the living cationic polymerization of monomers of varying reactivity, they require the removal of metal catalyst residues which are toxic and present a significant problem for potential commercial applications.

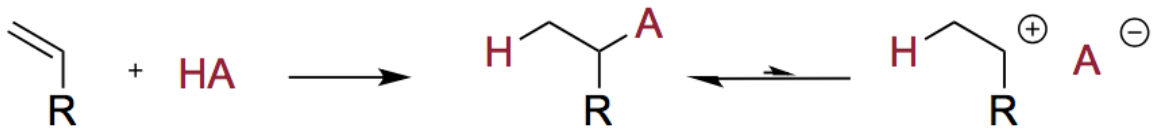


Figure 1. Initiation of cationic polymerization

Recently, Kamigaito and coworkers have reported examples of metal-free living cationic polymerizations that occur via a RAFT mechanism.[29-30] These studies have introduced a novel method to achieve controlled/living cationic polymerizations, that proceed through a cationic chain transfer mechanism analogous to that of conventional radical RAFT polymerization. Independently, and almost simultaneously, researchers working in the Nicewicz and the You group developed a novel method for the metal-free cationic photopolymerization of 4-methoxystyrene controlled by methanol. The system utilized a combination of 2,4,6-tri(p-toyl)pyrylium tetrafluoroborate as the photoinitiator and a small amount of methanol as the controlling agent.[31] The introduction of methanol into the polymerization system yielded polymers with both lower M_n (number average molecular weight) and Đ (dispersity) than the analogous system

without methanol. This discovery allowed for the initial hypothesis that the methanol additive was providing control over the system. After determining that the effect of the alcohol additive on the polymerization was nucleophilic in nature, additional studies were conducted to investigate the effect of methanol loading on the M_n and Đ of the system. The degree of methanol loading was shown to exhibit a strong influence over M_n and Đ, with increased methanol loadings associated with decreased M_n and Đ, while the pyrillium loading was shown to have a minimal influence on the M_n of the synthesized polymers. From these data and other kinetic studies, it was concluded that methanol acts as a reversible chain transfer agent, similar to the role of dithiocarbamates in reversible addition-fragmentation chain transfer (RAFT) free radical polymerization.[31]

The successful demonstration of the photo-initiated living cationic polymerization of 4-methoxystyrene mediated by methanol motivated us to further explore this exciting discovery of a mild, acid-free system for living cationic polymerizations. This investigation aims to expand the scope of the previous study to systems utilizing a traditional acid initiator. While the use of the photoinitiator resulted in successfully controlled reactions, its mechanism of initiation is complex, as evidenced by the induction period into the polymerization. A fast and simple initiation by protonic acids, which should exhibit no induction period, will allow us to focus on the mechanistic understanding of this unique living cationic polymerization. As mentioned previously, living cationic polymerizations utilizing super strong acids (TfOH) in combination with thiocarbonylthio compounds and thioethers have recently been reported by the Kamigaito group.[29] In both cases, the mechanism to achieve the "living" character of the polymerization was believed to be similar to that of conventional RAFT polymerization with the key intermediate being a sulfonium (S^+) species. However, to our knowledge, no alcohol mediated cationic RAFT polymerization initiated by protonic acid has been reported in the literature. Our study is a new contribution to the field of

cationic RAFT chemistry by introducing an oxonium (O^+) species as the key intermediate in the RAFT mechanism. The ultimate goal of our investigation is to further explore and establish an alcohol mediated living cationic polymerization, proceeding through a mechanism similar to that of radical RAFT polymerization. We will explore the mechanistic details of this new metal-free, protonic acid initiated and alcohol mediate living cationic polymerization and investigate how the nature of the cationic chain transfer agent will impact the living nature of the polymerization by expanding the system into thiols as simplistic sulfonium based chain transfer agents. This will potentially establish a simple and effective methodology for achieving living cationic polymerizations utilizing mild reaction conditions that allows for future innovations in polymer synthesis.

Experimental Details

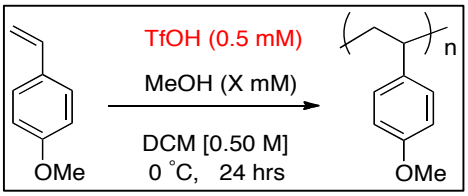


Figure 2. Reaction scheme for living cationic polymerization of styrene, 4-methylstyrene with triflic acid initiator and methanol catalyst.

Methods and Materials

Gel permeation chromatography (GPC) was carried out using a Waters Alliance 2695 instrument equipped with a refractive index detector (Waters 2414). Samples were passed through three columns (Waters Styragel HR5, HR4, and HR2) using THF as the mobile phase. All molecular weights (Mn, Mw) and molecular weights distributions (dispersities, Mw/Mn, Đ) were determined by calibration to known, standard polystyrene samples purchased from Polyscience Corporation. Proton magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker model DRX

400 spectrometer with internal standard. All reagents were purchased from Sigma-Aldrich corporation, Fisher Scientific corporation, or Acros corporation and were used without additional purification unless otherwise noted. Anhydrous dichloromethane was dried further over an activated alumina plug; 4-methoxystrene was distilled under calcium hydride before use and stabilized with tert-butbutylcatechol as an inhibitor;

Example standard polymerization of poly(4-methoxystyrene)

To a clean, oven-dried scintillation vial was added a Teflon coated stir bar, before being degassed and backfilled with Argon three times. Once under Argon atmosphere, the reaction vial was cooled to 0 °C. While stirring, anhydrous dichloromethane (2.7 mL) was added to the reaction vial using a 1 mL gas-tight syringe under a constant pressure of Argon. Deinhibited 4-methoxystyrene (200 μL, 1.51 mmol), followed by anhydrous methanol, were then added to the reaction mixture via a gas tight Hamilton syringe. Finally, a separate gas-tight syringe was used to add triflic acid stock solution to the reaction vial. The reaction mixture was stirred at 0 °C for 24 hours before trimethylamine (5 μL) was added to quench the polymerization. The synthesized polymer was precipitated into cold methanol and the resulting precipitate isolated by vacuum filtration. Any samples that were not able to be isolated via vacuum filtration were isolated via rotary evaporation. As much of the white, powder precipitate as possible was transferred to weighed scintillation vials, and dried overnight under high vacuum before analysis.

Sample Preparation

Samples for GPC were dissolved in THF at room temperature, prepared at a concentration of approximately 1 mg/mL. The solutions were allowed to stir for 30 minutes before being filtered

through a 0.2 TFE micron filter. All molecular weight and dispersity data are the average of three trials unless otherwise noted.

Results and Discussion

We commenced our study with an investigation into optimization conditions for the polymerization utilizing a constant initial concentration of monomer [M_0 = 500 mM] and methanol [MeOH = 5 mM], while systematically varying the acid loading, temperature, and time of the polymerization. Through these studies, it was determined that the polymerizations run at a temperature of -78°C, typical for cationic polymerization, yielded no polymers, even with high acid loadings (12.5 mM) and polymerizations run at -40 °C yielded polymers only at very high acid loadings (12.5 mM) and prohibitively long reaction times (>24 h). The optimal temperature condition was found to be 0 °C, which yielded polymer with well controlled molecular weights at all acid loadings (1 mM, 5 mM, 10 mM), as in the polymerizations run at room temperature a loss of control over molecular weight was observed. Subsequent experimentation indicated that, as expected, the time necessary for the reaction to reach full conversion was related to the amount of acid loading, with increased acid loadings resulting in shorter reaction times. Therefore, to ensure continuity between trials, polymerizations were run for 24 hours to achieve 100% conversion at all acid loadings.

After this comprehensive investigation for the optimization of polymerization conditions, we began our investigations using triflic acid as the proton source and methanol as the chain transfer agent in dichloromethane (DCM) as the solvent. Poly(4-methoxystyrene) of high molecular weight (M_n > 40 kg/mol) and broad molecular weight distribution (Đ > 2) was obtained when the conditions for a conventional acid initiated cationic polymerization were employed, omitting the methanol additive (**Table 1, line 1**). However, the addition of methanol to the system resulted in a decrease in both the molecular weight and the dispersity of the resulting poly(4-

methoxystyrene), suggesting that methanol may be acting to control the system.

Table 1. Alcohol Additive Study.

Entry	Additive	Mn (kg/mol)[a]	Đ [a]	Yield (%) [b]
1	--	20.31	2.37	94
2	MeOH	9.67	1.17	93
3	EtOH	12.51	1.36	97
4	i-PrOH	16.40	1.65	98
5	t-BuOH	19.03	1.95	95
6	CF_3CH_2OH	23.01	2.00	92

[a]Determined by GPC, relative to polystyrene standards, average of three experiments. [b]Yield after precipitation, average of three experiments

The effect of the methanol additive on the system was probed via proton NMR analysis of the synthesized polymers. The resulting NMR spectra indicated the presence of methoxy end groups at the chain termini. Resonances centered around δ 2.95 ppm were identified and found to be in agreement with methoxy-capped poly(4-methoxystyrene) synthesized utilizing the photo-initiated system (**Figure 3**). In further support of the formation of methoxy-capped poly(4-methoxystryene), no resonances were seen centered around the expected chemical shift for methanol of δ 3.49 ppm, confirming that the effect of methanol control is not due to precipitation of the polymer into methanol post polymerization. Additionally, resonances were observed centered around δ 1.00 ppm, indicative of a methyl end group. This methyl end group likely formed from initiation via protonation, providing strong evidence that the mode of propagation for the polymerization is cationic in nature.

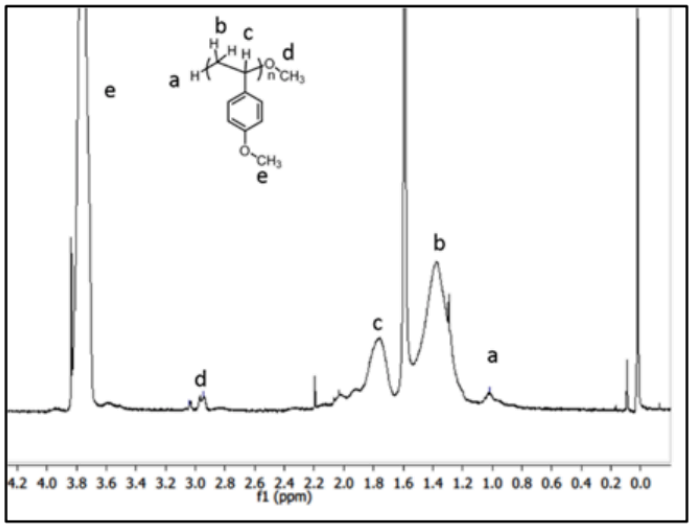


Figure 3. ^{1}H NMR spectra of poly(4-methoxystyrene) showing methoxy end groups at the chain termini.

The significant effect on the control of the polymerization via the addition of methanol as well as the prior results obtained from the photo-initiated system suggested a nucleophilic interaction between methanol and the propagating chain end. As such, the nature of the R and nucleophilicity of the alcohol group should significantly impact the control imparted by its addition. To confirm this hypothesis, a series of polymerization were carried out under identical conditions apart from the nucleophilicity of the alcohol additive used. The alcohols utilized, in order of decreasing nucleophilicity, were: methanol, ethanol, iso-propanol, tert-butanol, and trifluoroethanol. Based on the proposed mechanism and its reliance on nucleophilic attack of the carbocation chain by the alcohol additive, both the M_n and D of the synthesized polymers should be sensitive to the nucleophilicity of the added alcohols. As the nucleophilicity of the alcohols decreased, both the M_n and D of the resulting poly(4-methoxystrene) were seen to increase (**Table 1**). This trend is suggestive that there is a nucleophilic interaction between the alcohol additive and the propagating chain end. However, the decrease in the nucleophilicity of the alcohol additive is also concurrent with increased steric hindrance. To confirm that effect of the alcohol additive is

nucleophilic in origin rather than simply steric, trifluoroethanol, an alcohol of a similar steric environment around the hydroxyl group to ethanol but with decreased nucleophilicity was employed. A loss of control over the polymerization was observed when using trifluoroethanol rather than ethanol as the alcohol additive, the former being much less nucleophilic than ethanol due to the electron withdrawing character of the trifluoromethyl group. The observed loss of control despite the steric similarities and the decreased nucleophilicity of trifluoroethanol confirms that the effect of the alcohol additive is nucleophilic rather than steric in nature.

A detailed study was then undertaken to clarify the polymerization mechanism utilizing the protonic acid initiator. To understand the role of methanol in controlling chain length, and therefore molecular weight, the effect methanol and triflic acid loading were investigated at variety of conditions. The effect of methanol loading at constant TfOH concentrations were first investigated (**Figure 4**). As expected, in the absence of MeOH, the polymerization was uncontrolled, resulting in a broad distribution of molecular weights (Đ > 2). The MeOH concentration was then increased to values between 5 and 50 mM (5 mM, 10 mM, 20 mM, and 50 mM), while the monomer concentration, TfOH concentration, and reaction time were held constant (**Table 2**). A decrease in the molecular weight was observed as the loading of methanol was increased between 5 and 50 mM for acid loadings of 0.5 mM, 1 mM, 5 mM, and 10 mM, indicating a consistency in the trend. The addition of methanol lowered the M_n as well as narrowed the molecular weight distribution (as measured through the D), demonstrating its role in molecular weight control. For [TfOH] = 0.5 mM, an increase in the methanol concentration between 5 and 50 mM resulted in a decrease in the molecular weight **(Figure 4a).** The same trend of decreasing molecular weight with increasing concentration of MeOH was also observed for [TfOH]= 1 mM and [TfOH]= 5 mM (**Figure 6**), which suggests that methanol likely plays a key role in the number

of chains initiated. Additionally, the observed experimental molecular weights are in good agreement with the theoretical molecular weights calculated assuming that each molecule of MeOH generates one polymer chain.

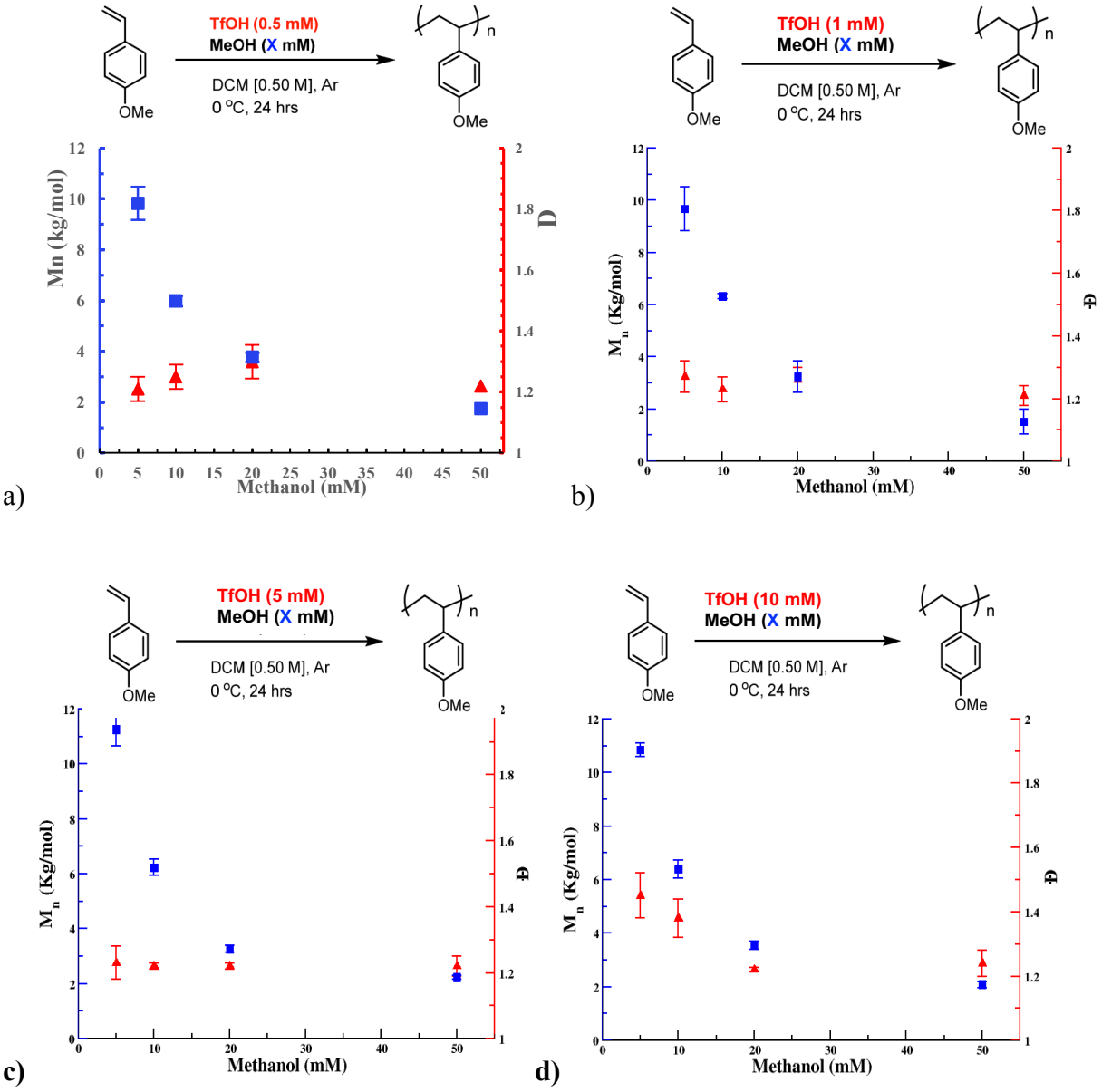


Figure 4. Effect of methanol loading on M_n and Đ of poly(4-methoxystyrene). All data were obtained as the average of 3 experiments, Mn and Đ determined by GPC, relative to polystyrene standards. Conditions: a) 0.5 mM TfOH, b) 1 mM TfOH, c) 5 mM TfOH, d) 10 mM TfOH

Table 2. Effect of MeOH Loading on Control of Polymerization Results

TfOH (mM)	MeOH (mM)	Mn[a] (Calc.) kg/mol	Mn[b] (GPC) kg/mol	Đ[b]
10	–		13.85	3.50
10	5	13.41	10.85	1.45
10	10	6.70	6.40	1.38
10	20	3.37	3.55	1.22
10	50	1.34	2.09	1.24

[a] Calculated based on the assumption that each polymer chain is terminated by one molecule of methanol [b]Determined by GPC, relative to PS standards, average of 3 experiments

These data were then examined to determine the effect of increased acid loading on the molecular weight, while the concentrations of MeOH and monomer are held constant. While changes in the methanol concentration had a significant effect on the $M_{n,}$ when the MeOH concentration was held constant at 5 mM, increases in the acid loading from 1 to 5 to 10 mM had a relatively small influence on the M_n and Đ of the resulting polymers **(Figure 5**). Similar results were obtained for varied MeOH concentrations (5 mM, 20 mM, 50 mM), with synthesized polymers exhibiting low Đ around 1.2 and minimal increases in M_n at larger loadings of TfOH **(Figure 5).** These data suggest that it is solely methanol, rather than the TfOH that imparts control in the reaction mechanism.

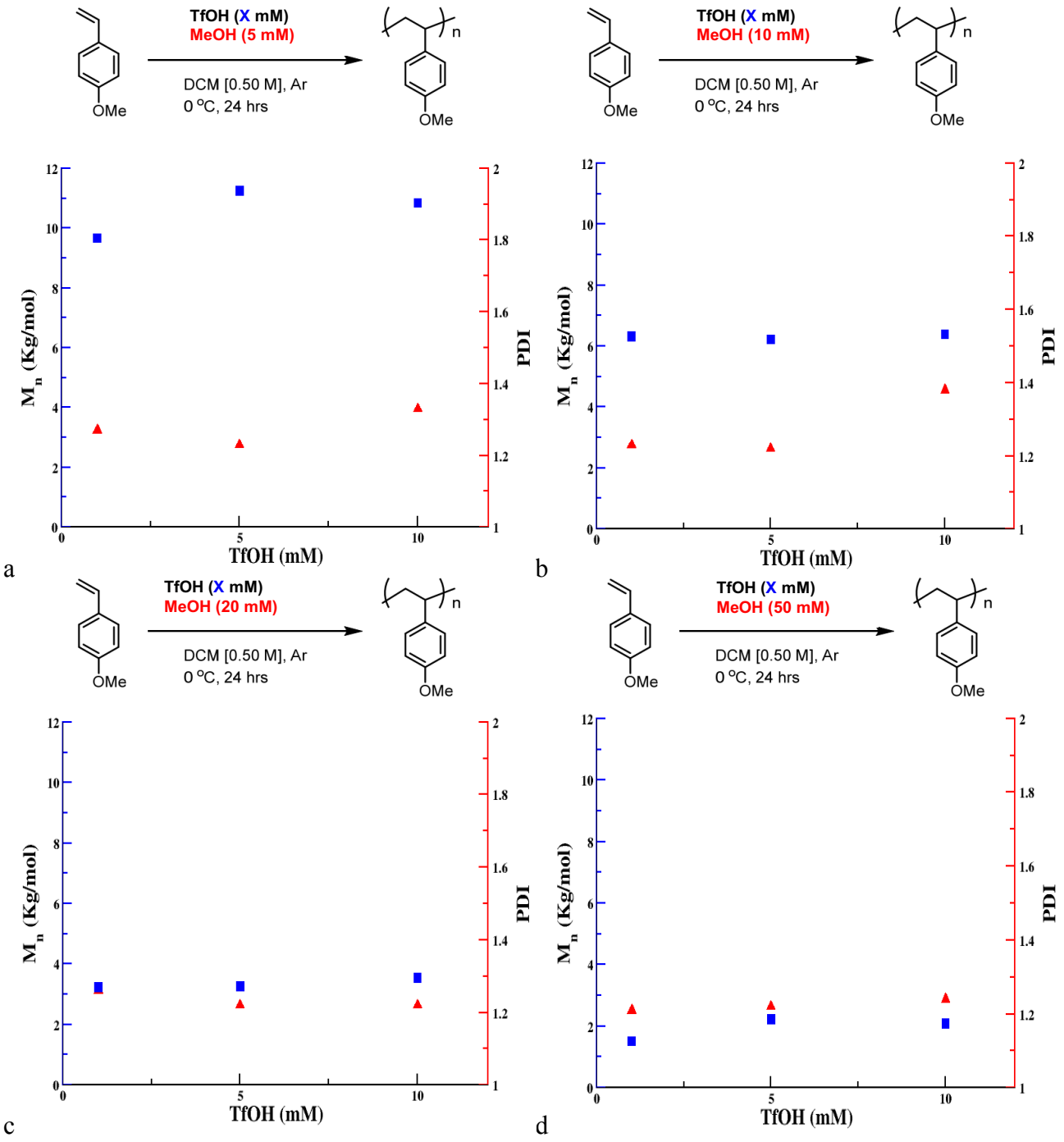


Figure 5. Influence of loading of TfOH on M_n and Đ of poly(4-methoxystyrene). All data were obtained as the average of 3 experiments, Mn and Đ determined by GPC, relative to polystyrene standards. Conditions: a) 1 mM MeOH, b) 5 mM MeOH, c) 20 mM MeOH, d) 50 mM MeOH

Proposed Mechanism

Based on these preliminary results and observations, we propose a plausible mechanism for this living cationic polymerization initiated by a protonic acid and mediated by methanol (Scheme 1). This new living cationic polymerization is mechanistically analogous to radical RAFT but utilizes methanol as a simpler chain transfer agent rather than the traditional substituted thiocarbamates. Triflic acid acts as the protonic initiator, which generates a styrenyl cation as the propagating carbocation species by protonating the monomer in solution (**Scheme 1, i**). The use of the strong protonic acid provides fast initiation and eliminates the induction period before propagation of the chains occurs. Once a carbocation has been generated, methanol undergoes nucleophilic addition to the carbocation species and generates an additional proton capable of protonating another monomeric unit (**Scheme 2, ii**). The newly protonated monomer can then also undergo nucleophilic attack by methanol creating a cycle of rapid chain transfer that continues until all methanol has been converted into methoxy endgroups with very few active chain ends remaining (**Scheme 2, ii**). This proposed mechanistic step accounts for the prior data that indicates the concentration of methanol determines the number of chains activated rather than the concentration of initiator.

The key step to achieve the living character of the polymerization is the Reversible Addition-Fragmentation Chain Transfer (RAFT) via an oxonium intermediate (**Scheme 2, iii**). The methoxy endgroup of the dormant polymer chains acts as the chain transfer agent by forming a stable oxonium ion intermediate via nucleophilic capture of a propagating carbocation chain end. As the majority of chain ends in solutions are capped with a dormant methoxy group, there are few active oxonium intermediates in solution at one time. Due to a fast equilibrium favoring the dormant chains, the resulting oxonium intermediates rapidly dissociate via heterolysis of either of the two carbon-oxygen bonds, generating an active carbocation chain and a dormant methoxy-capped chain. The active chain can then propagate until it recombined with the methoxy endgroup

of another dormant chain. This nucleophilic recombination regenerates an oxonium intermediate capable of undergoing further fragmentation and recombination. The transient formation of the oxonium intermediate provides a fast activation/deactivation process between the active and dormant species, where the majority of chains remain dormant and propagation is well controlled. This control over propagation imparts control over both molecular weight and dispersity.

Given that this cationic RAFT mechanism is analogous to that of radical RAFT, the polymerization should be considered "living" in that the chain ends remain active even after all initial monomer has been consumed. To verify the living nature of the polymerization, chain extension studies were conducted. After 100% conversion of initial feed monomer had completed, verified via proton NMR analysis, an additional equivalent of monomer was added to the reaction mixture. GPC analysis indicated a monomodal shift toward higher molecular weight, while maintaining a narrow D (**Figure 6**). The almost doubling of molecular weight from the mother polymer to the chain extended polymers and the narrow D value, are indicative that the chain ends remain active after initial consumption of monomer and that the polymerization can be considered living.

The main principle behind the proposed mechanism is the nucleophilic attack of the propagating carbocation by the chain transfer agent. As such, other nucleophilic species, such as thiols, should be able to act as the chain transfer agent and go through a similar mechanism to enable the "living"/ controlled polymerization. The resulting sulfonium intermediate is similar to those generated through the use of traditional RAFT thiocarbamate chain transfer agents, but through a simpler, more cost-effective mode. Methanethiol is the best analog to methanol and would be the ideal sulfur based chain transfer agent for these cationic studies, but it too volatile to be effectively used. As such, propanethiol (PrSH) was initially studied as a potential chain transfer agent (**Figure 7**).

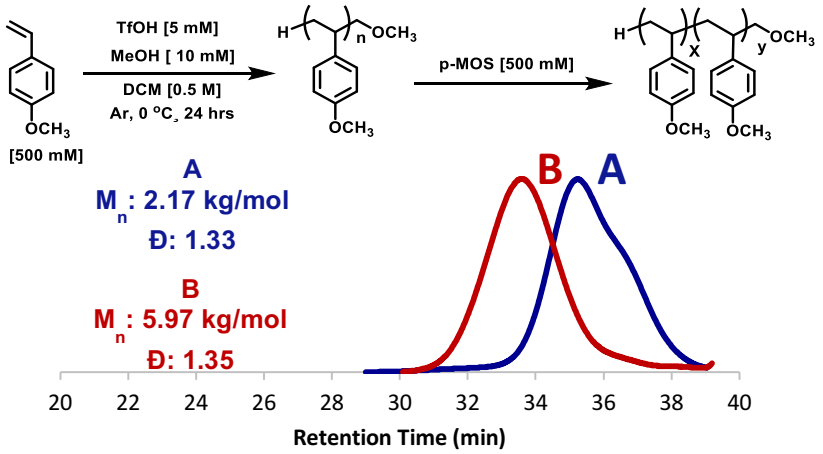
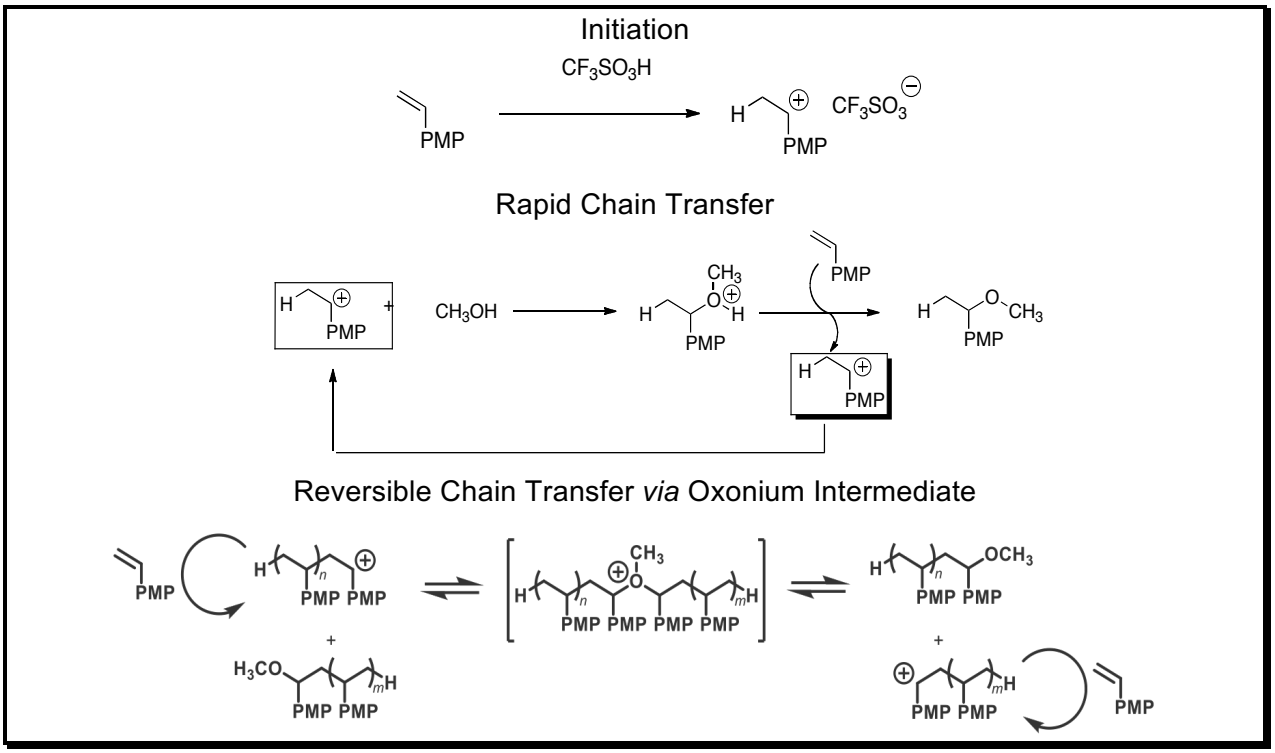


Figure 6. GPC traces showing a monomodal shift toward a high molecular weight after addition of monomer.



Scheme 1. Mechanistic proposal

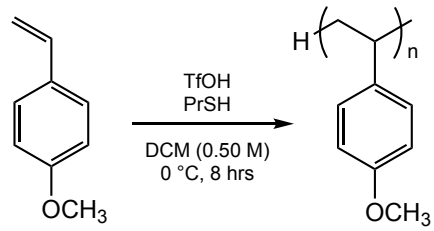


Figure 7. Reaction scheme for living cationic polymerization of styrene, 4-methylstyrene with triflic acid initiator and propanethiol additive.

Initial trails were then run to investigate the effect of the thiol loading at constant concentration of TfOH to determine if it acts in an analogous role to methanol. The PrSH concentration was varied at 5, 10 and 50 mM, while the Triflic acid loading was kept constant at 0.5 mM (Table 3). A decrease in the molecular weight was observed as the loading of PrSH was increased, similar to the trend seen in the MeOH trials (**Figure 8**). However, there is less agreement at lower PrSH loadings between the experimental molecular weights, determined via GPC, and the theoretical molecular weights calculated under the assumption that each molecule of PrSH generates one polymer chain as the proposed mechanism suggests. Despite the lack of good agreement at lower loadings of PrSH, the lower Đ values of the synthesized polymers (Đ < 1.3), indicate that the reaction is controlled. These initial data that show a decrease in the molecular weight as the loading of PrSH is increased suggests that the PrSH is acting to control the number of active chains within the reaction and therefore the molecular weight.

Table 3. Polymerization Results utilizing Propanethiol as Chain Transfer Agent

	TfOH (mM)	**PrSH (mM)**	**Mn[a] (Calc.) kg/mol**	**Mn[b] (GPC) kg/mol**	**Đ[b]**
A	0.5	5	13.14	6.63	1.22
B	0.5	10	6.7	5.65	1.22
C	0.5	50	1.34	1.35	1.17
D	0.5	5	13.14	7.46	1.31
E	0.5	10	6.7	5.49	1.24
F	0.5	50	1.34	1.38	1.11

M_n values both experimentally determined and calculated for [TfOH]=0.5mM [a] Calculated based on the assumption that each polymer chain is terminated by one molecule of methanol [b]Determined by GPC, relative to PS standards.

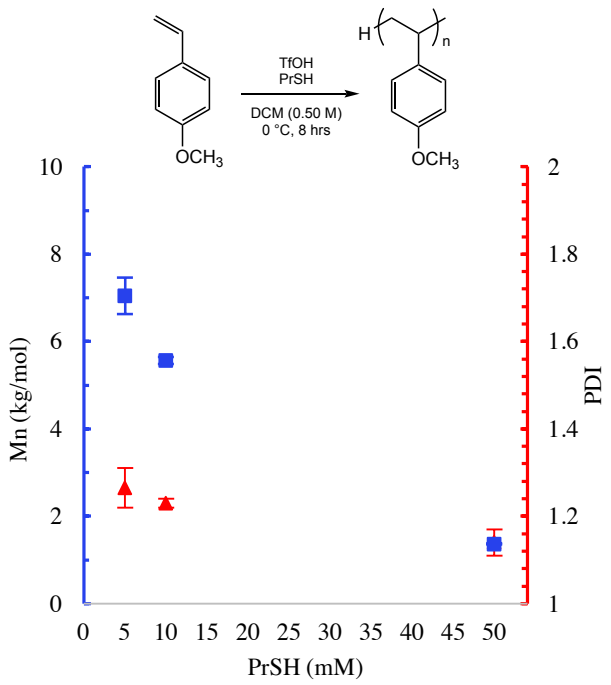


Figure 8. Effect of propanethiol loading on M_n and Đ of poly(4-methoxystyrene). All data were obtained as the average of 3 experiments, Mn and Đ determined by GPC, relative to polystyrene standards. Conditions: 0.5 mM TfOH

Studies were also conducted using PrSH to determine the effect of TfOH loading on the molecular weight and dispersity of the resulting polymers. For a PrSH concentration equal to 10 mM, increases in the acid loading from 1 to 5 to 10 mM had a non-negligible effect on the molecular weight. Unlike the MeOH system, increases in the concentration of TfOH resulted in larger dispersity values as well as lower molecular weights (**Figure 9**). These initial data must be reproduced for further conformation, but suggest that there may be some effect from the TfOH on the control of the polymerization in the thiol system that is not present in the MeOH system. Based on the studied utilizing propane thiol and the prior investigations on the effect of the nucleophilicity of the alcohol additive on the control of the system, we desired to study the effects of a longer, less nucleophilic thiol on the control of the system.

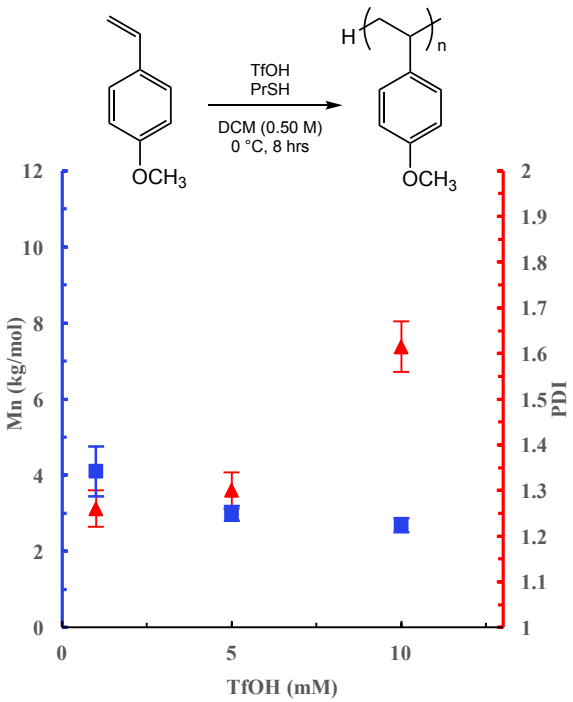


Figure 9. Effect of TfOH loading on M_n and Đ of poly(4-methoxystyrene). All data were obtained as the average of 3 experiments, Mn and Đ determined by GPC, relative to polystyrene standards. Conditions: 10 mM PrSH

Decanethiol was then utilized as a chain transfer agent to test the impact of the thiol additive itself on the mechanistic control (**Figure 10**). Initial studies were run to see if decanethiol presented the same trends of a loss of control as TfOH loading in the system was increased. Preliminary data indicates that the loss of control when utilizing decanethiol as the chain transfer agent is not as pronounced as when propanethiol is used as the chain transfer agent (Table 4). There remains a small increase in the dispersity as the loading of TfOH is increased, but it is less than that seen in PrSH. These data indicate that, despite the lessened nucleophilicity of decanethiol as the chain transfer agent, there is potentially an increase in the control of the reaction. These data are preliminary, but suggest that the thiol based chain transfer agent system differs than that of the methanol mediated system.

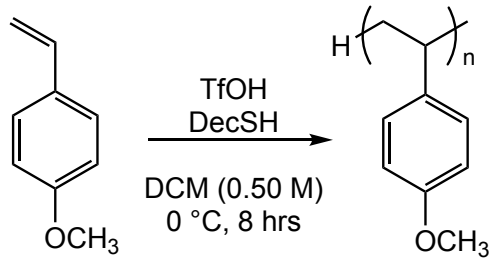


Figure 10. Reaction scheme for living cationic polymerization of styrene, 4-methylstyrene with triflic acid initiator and decanethiol additive.

Table 4. Polymerization Results utilizing Propanethiol as Chain Transfer Agent

	TfOH (mM)	**PrSH (mM)**	**Mn[a] (Calc.) kg/mol**	**Mn[b] (GPC) kg/mol**	**Đ[b]**
A	1	10	6.7	5.34	1.26
B	5	10	6.7	4.31	1.37
C	10	10	6.7	4.24	1.34

M_n values both experimentally determined and calculated for [TfOH]=0.5mM [a] Calculated based on the assumption that each polymer chain is terminated by one molecule of methanol [b]Determined by GPC, relative to PS standards.

Conclusions and Summary

We have carried out initial studied into the metal free acid-initiated living cationic polymerization of 4-methoxystyrene using methanol as an alcohol additive. The continued polymerization upon monomer addition from chain extension studies as well as the narrow Đ values obtained indicate the controlled/living nature of the polymerization. Investigations into the effect of methanol and TfOH loading on the control of the reaction suggest that methanol plays a key role in the control of the polymerization and that for the methanol system the loading of TfOH does not affect the control of the reaction. Based on the collected data, we have proposed that the mechanism of the polymerization follows a cationic RAFT mechanism, analogous to that of radical RAFT, where methanol acts as the reversible chain transfer agent. The control of the

polymerization is imparted via the reversible activation and deactivation of an oxonium intermediate generated through nucleophilic attack of the alcohol additive on the propagating cationic center. Studies of alcohol nucleophilicity indicate that the control of the reaction is inversely related to nucleophilicity of the alcohol additive, with stronger nucleophiles providing in a greater degree of control over the reaction. Given this nucleophilic control, thiols were explored as a potential chain transfer agent. Propane thiol presented similar results to the methanol system, with preliminary data suggesting that propanethiol rather than TfOH imparts control over the reaction. Preliminary trials with decanethiol indicate that there may be a loss of control with increasing acid loading not seen in the methanol or propanethiol studies, indicating the thiol based system may not adhere to the same mechanistic pathway as the methanol system. Further studies will be conducted utilizing decanethiol to support or refute these initial data.

Further development of this methodology will focus on elucidating the kinetics of the methanol mediated system to determine whether first order kinetic behavior is observed. Additionally, expansion of the scope of this methodology to further monomers has been initiated but will be developed more fully in the future. Given the controlled, living nature of the polymerization, future goals are to extend the synthetic methodology to the preparation of block copolymers and polymers or more complex architectures that could previously not be achieved.

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